# EVALUATION OF COMBINATION FUELS FOR FLUIDIZED BED COMBUSTORS BY THERMAL ANALYTICAL TECHNIQUES

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#### ABSTRACT

The objective of this study is to find suitable combinations of coal fines, municipal solid waste (MSW), and limestone to produce fuel pellets for fluidized bed combustion systems. The coal fines, MSW (paper), and sorbent limestone were mixed in different combinations and the volatile matter and char contents of all mixtures, as well as the original materials, were evaluated by thermogravimetric analysis (TGA). Using different rates of heating and variable atmospheres, information was obtained that can be useful in predicting the combustion behavior and efficiency of the combination fuels. Optimum limestone content can be determined by selectively introducing CO<sub>2</sub> during the final stages of the combustion process to check for excess CaO. The use of combined techniques such as TGA, differential thermal analysis (DTA), and TGA-FTIR can be utilized to determine detailed information on the combustion and thermal properties of the combination fuels.

## INTRODUCTION

More than 150 million tons of municipal solid waste (MSW), are generated in the United States each year. This excessive amount of generated waste, combined with decreases in landfill sites, causes serious environmental problems and forces the establishment of programs for reducing the volume of waste deposited in landfills.

Mass burning of unprocessed MSW and preparation/firing of refuse-derived fuel (RDF), are the two main methods currently being evaluated for waste-to-energy technologies (1,2). There are several methods used for the firing of RDF. The chief method employed in this study is fluidized bed combustion. Fluidized bed combustion systems are particularly suited to waste fuels because of their ability to burn low grade and variable fuels as well as absorb sulfur oxides through the use of sorbents.

Fluidized bed combustion systems have been constructed in the U.S., Europe, and Japan, for the burning of RDF alone or combinations of RDF and wood waste (3). However, there is little or no information available regarding RDF firing in the presence of coal in fluidized bed combustion systems, or co-firing of wood wastes with coal. There have been several studies conducted on the preparation of fuel

pellets using coal fines and limestone, which serves as a sorbent for sulfur oxides (4-6). This information was valuable in the evaluation of the combustion performance of fuel pellets prepared from coal fines, MSW or wood waste, and limestone sorbent.

The burning profiles of coal and RDF are quite different, but there is a high probability that blends of these two fuels, when co-fired under the right conditions, perform suitably as a boiler fuel. This conjecture forms the basis of the study reported in this paper.

In general, normal production of coal yields millions of tons of coal fines each year (about 20% of total yield). These fines, however, can not be sold because of handling problems. The cost of recovery of these fines is small compared to the mining of coal. Coal fines are an excellent source of an energy-rich fuel that can be blended with RDF to produce pellets suitable for use in fluidized bed combustion systems.

When coal contains high amounts of organic sulfur it is impossible to remove the sulfur using conventional physical cleaning methods. Fluidized bed combustion systems utilizing coal-limestone-fuel mixtures have the potential for resolving this limitation since limestone, which is abundant in nature, can be used as a sorbent for emitted SO<sub>2</sub>.

## SAMPLE PREPARATION AND RESULTS

#### Thermal Analysis of Raw Materials

The materials used for this study are coal fines (Illinois #6), Kentucky agricultural limestone, and newspaper. All samples were prepared and analyzed in Western Kentucky University's Coal and Fuel Characterization Lab. The three materials were studied by thermogravimetric analysis (TGA) to assess their thermal behavior. The TGA experimental conditions used were 10 mg sample size, air atmosphere with a flow of 50 mL/min, and a heating rate of 20°C/min. The instrument used was a Shimadzu HT 1500 TGA Thermogravimetric Analysis System.

Test results for the three materials are shown in Figure 1. The TG curve for coal depicts two weight loss stages, the first consisting of a 3.09% moisture loss followed by a second weight loss of 85.25% containing two overlapping DTG peaks. The first DTG peak is a result of the combustion of aliphatic materials in coal and the second is due to the combustion of the aromatic materials of coal.  $T_{\rm Max1}$  and  $T_{\rm Max2}$  occur at 417°C and 440°C, respectively.

Figure 1 also shows two decomposition stages for limestone. There is an initial moisture loss of 1.73% beginning at 397°C and a second weight loss of 40.95% beginning at 563°C. This is due to limestone being converted to CaO and Co<sub>2</sub> gas.  $R_{\text{Max}}$  (mg/min), was 0.76 at 817°C. Experimental conditions were identical to that used for coal.

Finally, Figure 1 represents three major weight loss stages for newspaper with the first being a moisture loss of 4.35%. The second weight loss of 88.57% represents the major decomposition of materials in newspaper and has an  $R_{\rm Max}$  of 5.34 at 353°C. The overlapping peak is shown on the DTG curve and represents the decomposition of impure cellulosic materials with higher lignin content in the newspaper. The third and last weight loss phase of 5.91% is due to char gasification and has a small peak at 475°C. Experimental parameters were again identical to those used in the TG analysis of coal. It is evident from the TG curve that newspaper decomposes 150°C earlier than coal. Total weight losses of

coal, limestone, and newspaper (established on a moisture free basis), were 88%, 42.7%, and 98.8%, respectively.

1

# Thermal Analysis of Coal-Limestone Mixtures

In order to decide upon an optimum amount of limestone for the combination fuels for the fluidized bed combustor, mixtures of coal and limestone were tested by TGA. Testing procedures preceding  $800.850^\circ\text{C}$  were identical to those previously examined. However, after  $800^\circ\text{C}$  or  $850^\circ\text{C}$ , temperatures were held constant for 5 minutes, the atmosphere was changed to  $CO_2$  gas for 25 minutes, and a determination was then made as to the amount, if any, of weight gain that occurred (See Figure 2). If a weight gain did occur, this indicated that an excess of CaO was in the residue and was converted back to  $CaCO_3$  when the  $CO_2$  was added. If a weight gain did not occur, this indicated that all of the CaO reacted with the  $SO_2$  to produce  $CaSO_4$ , leaving no excess CaO in the residue. This method was developed by R.F. Culmo and R. L. Fyans (7).

Next the optimum temperature at which the  $l_1^2$  mestone completely decomposed needed to be determined. A 5% limestone, 95% coal mixture was used to obtain the suitable temperature values. The TG results show that there is no significant weight changes above 800°C. Therefore 800°C and 850°C were chosen for the isothermal temperature values for test runs.

Using the chosen optimum temperature values, the optimum limestone percentage needed to be determined. To accomplish this goal, different percentages of limestone (0,1,2,3,4,5, and 10%), were added to the coal. The results of these tests, as shown in Figure 3, indicate a suitable limestone percentage is between 1% and 3%. A plateau in the weight gain curve occurs between 1-3% and increases significantly with increased amounts of limestone (excess CaO). Thus, 2% limestone was chosen for the following study. It should be recognized that excess limestone will reduce the flame temperature in the fluidized bed combustion system and also increase the operational costs.

Considering that the heating rate is higher in fluidized bed combustors than that used in the experimental tests used thus far, higher heating rates for tests were chosen to observe the effect heating rates may have on the decomposition of the fuel mixtures. Heating rates of 20°C/min, 35°C/min, 40°C/min, and 50°C/min were chosen for additional experiments. These heating rates were used with 2%, 5%, and 10% limestone percentages. The TG results indicate the weight gain, due to absorbed SO<sub>2</sub>, at different heating rates and limestone percentages was not significantly affected under these specific experimental conditions.

A determination of the change in weight loss during combustion as a function of varying coal-limestone mixtures was made. It was determined that the 2% limestone did not show any catalytic effect on the first thermodecomposition stage of coal. Similar results were obtained for the second thermodecomposition stage.

Finally, the effect of limestone on the thermal behavior of the mixture with respect to changes in the parameters  $T_{\rm max}$  and  $R_{\rm max}$  was determined. The TG results indicate that at heating rates of 20°C/min and increased limestone content,  $T_{\rm Max1}$  and  $T_{\rm Max2}$  shift to slightly higher temperatures. The TG curve also shows that  $R_{\rm Max1}$  and  $R_{\rm Max2}$  slightly decrease with increased limestone percentage. Both TG curves present the same results; higher limestone content may delay the decomposition and combustion slightly as  $T_{\rm Max}$  increases and  $R_{\rm Max}$  decreases.

# Thermal Analysis of Combination Fuels

The combination fuels tested consist of coal, limestone, and newspaper (RDF), in varying percentages. According to the results of the preliminary (RDF)

studies, it is believed that a 2% limestone content in the mixture is sufficient for absorbing the  $SO_2$  emitted for the burning of the coal tested. The mixtures of coal, limestone, and newspaper are 90/2/8, 80/2/18, and 70/2/28, respectively.

The general TG curve of the combination fuel is shown in Figure 4. There were four thermodecomposition stages observed, excluding the moisture loss. The  $T_{\rm Max}$  for each stage was 283, 384, 450, and 489°C. It is believed that the first and second stages are due to the decomposition of newspaper, with the first being mainly due to cellulosic materials and the second to lignin content. Previously, Figure 1 indicated that there was one overlapping DTG peak with  $T_{\rm Max}=352^{\circ}{\rm C}$ . In the case of the combination fuel, however, the overlapping peak noted in Figure 1 became two separate peaks, and the first peak occurred 70°C earlier than noted for the newspaper alone. This may be due to reduced sample particle size that occurred during the grinding and preparation of the combination fuel. The third and fourth decomposition stages are due to the thermodecomposition of coal. However, the third stage was enhanced by two possible factors: (1) additional char gasification from the newspaper and/or (2) catalyzation of the char gasification by the limestone. The results for  $T_{\rm Max}$ ,  $R_{\rm Max}$  versus newspaper content are shown in Table 1.

To better understand and further verify the proposed mechanisms involved in the TG curve analysis, 50% coal/50% newspaper, 50% newspaper/50% limestone, and 50% coal/50% limestone test mixtures were also studied.

The TG and DTG curves of the 50% limestone/50% newspaper indicate three thermodecomposition stages with the first two peaks being due to the thermodecomposition of newspaper. The third peak was due to the decomposition of limestone.  $T_{\text{Max}}$  for peak one did not significantly change compared to that for 100% newspaper.  $R_{\text{Max}}$ , however, decreases by 20%.  $T_{\text{Max}}$  of peak two did not show any significant change. However the value of  $R_{\text{Max}}$  was five times greater than 100% newspaper. This might be due to the catalytic effect on char gasification. It is presently unknown why the third peak shifted  $10^{\circ}\text{C}$  earlier than 100% limestone; however,  $R_{\text{Max}}$  values were similar.

One may assume that the experimental values such as those listed in Table 2 may be used to predict the effects of varying amounts of limestone by utilizing known decomposition values for pure limestone and pure newspaper. However, in this case, there were significant differences between calculated (predicted) values and those obtained through experimentation. The first peak was retarded by the calcium, yielding lower weight loss values, and the second peak is influenced by a catalytic effect from the calcium. The third weight loss phase, however, was not effected because it was only due to the decomposition of limestone.

The TG results for 50% coal/50% limestone showed two thermodecomposition stages. The first peak, a combination of two overlapping peaks, shifted  $20\,^{\circ}\text{C}$  higher than that for  $100\,^{\circ}\text{C}$  coal. Again, the third peak, due to the thermodecomposition of limestone, occurred  $20\,^{\circ}\text{C}$  lower than that for  $100\,^{\circ}\text{C}$  limestone. Likewise,  $R_{\text{Max}}$  for peak one was reduced by 50% compared to that for  $100\,^{\circ}\text{C}$  coal. The TG results of 50% coal/50% newspaper showed three thermodecomposition stages with the first peak being due to newspaper, the second peak due to coal, and the third peak due to char gasification combined with less combustible materials from coal.

From reactivity studies, it can be concluded at this point in the analysis that the addition of limestone retarded the decomposition of coal and newspaper in the early stages, and then promoted the char gasification in the later stages due to the catalytic effect of calcium.

Ongoing research with combinations of TGA-FTIR and DTA techniques will provide a better understanding of the overall decomposition and combustion processes for coal-RDF-limestone fuels.

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 $\label{eq:Table 1} T_{\text{Max}} \text{ and } R_{\text{Max}} \text{ vs. Newspaper Content}$ 

	8% Newspaper	18% Newspaper	28% Newspaper
T <sub>Max1</sub>	283	290	287
T <sub>Max2</sub>	384	385	384
T <sub>Max3</sub>	450	451	454
T <sub>Max4</sub>	489	490	492
R <sub>Max1</sub>	1.66	2.20	2.68
R <sub>Max2</sub>	2.12	2.08	1.92
R <sub>Max3</sub>	1.29	1.29	1.60
R <sub>Max4</sub>	0.53	0.49	0.49

Table 2
Calculated Values for Weight Loss of 50% Newspaper/50% Limestone

Temp.°C	Tested Values %	<u>Calculate</u> Newspaper	ed Values Limestone	Difference %
150-381	37.05	.42.12	0.015	-5.09
381-539	13.16	3.10	0.825	9.24
539-800	20.77	0.10	20.5	_0.17
Total	71.04	49.4	22.1	-0.46

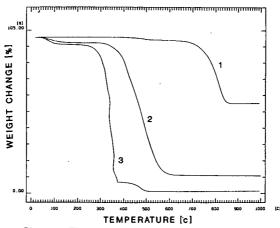


Figure 1. The TG Curves of three original samples 1-limestone; 2-coal; 3-newsprint;

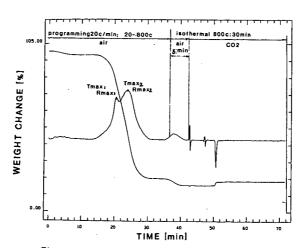


Figure 2. TGA analysis of coal/limestone mixtures

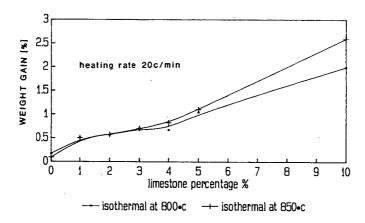


Figure 3. Weight gain vs. limestone percentage

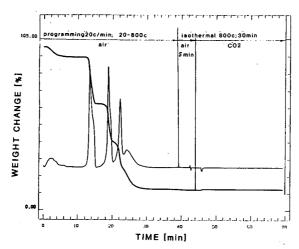


Figure 4. TGA analysis of combination fuels(C+L+N)